Pilot Testing of Oxidation Catalysts for Enhanced Mercury Control by Wet FGD

Paper # 36

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ABSTRACT

This paper presents results from two projects co-sponsored by U.S. Department of Energy's National Energy Technology Laboratory (DOE-NETL), and EPRI. The first project is being hosted and co-sponsored by Great River Energy (GRE) and City Public Service (CPS) of San Antonio, while the second is to be co-sponsored and hosted by TXU Energy and Duke Energy. The two projects are evaluating catalysts that oxidize elemental mercury (Hg^0) in flue gas to promote high mercury removal percentages in wet FGD systems. The paper presents results from over 20 months of mercury oxidation catalyst pilot unit operation at GRE's Coal Creek Station, including short-term pilot FGD tests to document the ability to remove catalytically oxidized mercury in a wet scrubber, and from 8 months of oxidation catalyst pilot unit operation at CPS' Spruce Plant. Results presented include mercury oxidation across the catalysts as a function of time in service, mercury removal across the pilot wet FGD, and other performance results such as flue gas pressure drop across the honeycomb catalysts. Planned work at TXU Energy's Monticello Steam Electric Station and at a bituminous coal-fired site is also described.

INTRODUCTION

A test program co-sponsored by EPRI and DOE-NETL has recently concluded at GRE's Coal Creek Station, as part of Cooperative Agreement DE-FC26-01NT41185, "Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems." The mercury control process under development uses catalysts to promote the oxidation of Hg^0 in flue gas from coal-fired power plants equipped with wet FGD systems. The oxidization reactants are already present in the flue gas and may include chlorine, hydrochloric acid, oxygen and/or other species. Oxidized mercury is removed in the wet FGD absorbers and leaves the system with the FGD byproducts.

The objective of the project is to test catalysts identified in a previous DOE-NETL co-funded project[1] at a larger scale and in a commercial form, so as to provide engineering data for future full-scale designs. The pilot-scale tests are to continue for over a year each site, to provide longer-term catalyst life data.

URS Group, Inc. is the prime contractor; EPRI is a co-funder of the current efforts and funded the initial development of the catalytic oxidation process. Two utilities are providing co-funding and host sites for this project: GRE, which fires North Dakota lignite at their Coal Creek Station (CCS) and CPS of San Antonio, which fires Powder River Basin (PRB) subbituminous coal at their J.K. Spruce Plant. These two host sites each have existing wet FGD systems downstream of high-efficiency particulate control devices.

The oxidation catalyst technology would have the greatest effect on scrubbed flue gas from lignite or subbituminous coal, where most of the mercury is present as Hg^0. While the current project includes testing at both a North Dakota lignite and a PRB site, both of which produce mostly Hg^0 in their flue gases, there are a number of scrubbed plants that fire Texas lignite, which also produces mostly Hg^0 in the flue gas. Also, some plants that fire bituminous coal may require additional Hg^0 oxidation to allow mercury capture in their FGD systems at high efficiency. A new project, Cooperative Agreement DE-FC26-04NT41992, adds two new sites to the current project, TXU Energy's Monticello Station, which fires Texas lignite, and a bituminous coal site. The existing pilot units in use at CCS and Spruce Plant will be moved to the new sites and charged with fresh catalysts for long-term catalyst activity tests there.

Also as part of the new project, a pilot-scale wet FGD system has been built. The mobile, pilot wet FGD will be used to verify the ability to scrub catalytically oxidized mercury at each of the four oxidation catalyst pilot test sites.

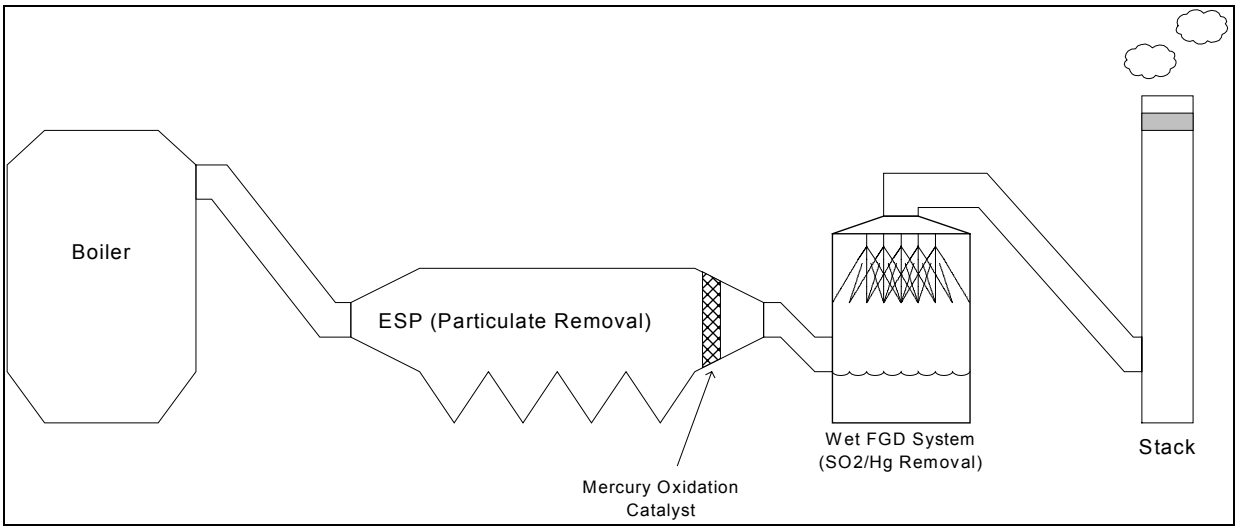
This paper covers the pilot test results from over 20 months of oxidation catalyst operation at the CCS site, including end-of-test wet FGD results from downstream of two catalysts and in situ catalyst regeneration tests. Also presented are the results from approximately 8 months of operation at Spruce Plant, and an overview of planned testing at the two new sites. A summary and interim conclusions are made at the end of the paper.

PROJECT DESCRIPTION

Figure 1 illustrates a simplified process flow diagram for the catalytic oxidation process, which is very straightforward and has no "moving parts." A catalyst, most likely in honeycomb form, is inserted into the flue gas path upstream of the FGD system. The outlet of the plant's cold-side particulate control device is a likely location for the catalyst, for two reasons. One is that the flue gas velocity is typically low there (e.g., about 5 ft/sec for an electrostatic precipitator [ESP]). This low velocity provides ideal conditions to operate a catalyst at longer residence time and low pressure drop. The other is that with the flue gas being relatively particulate-free, a close-pitched catalyst can be used. This allows for a high surface area per volume of catalyst relative to "dirty" gas operation, and allows less catalyst volume to be used. Downstream of the catalyst, the oxidized mercury is scrubbed in the FGD absorber, and leaves with the FGD byproduct.

Preliminary cost estimates showed that a catalytic process, if installed upstream of a wet FGD system, could allow plants to achieve 80 to 90% overall mercury control at a cost that is as much as 50% less than by injecting activated carbon.[1] However, the cost of the process will depend largely on the catalyst life and required catalyst volume. This project is collecting data that will allow these parameters to be evaluated for several coal types.

Figure 1: General Process Flow Diagram for the Mercury Catalytic Oxidation Process



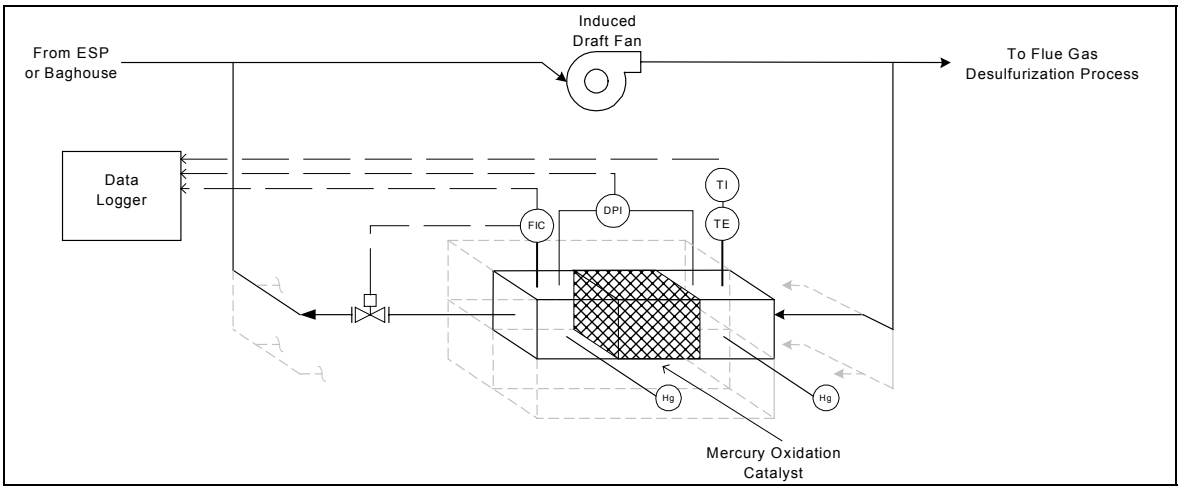
At each site, four different catalysts are being tested in parallel in a divided reactor sized to treat approximately 8000 acfm of flue gas (2000 acfm to each catalyst). This allows enough catalyst in each reactor to avoid "wall affects" that could significantly affect results. The pilot reactor treats low-dust flue gas from downstream of the ESP (CCS) or baghouse (Spruce), isokinetically extracted from the unit's induced draft (ID) fan outlet. The treated flue gas returns to the host unit's ID fan inlet, thus avoiding the need for a fan on the pilot unit. The amount of flue gas treated by the pilot unit is a very small fraction of the overall host unit flue gas flow, so this small amount of flue gas "recycle" does not cause adverse effects.

Figure 2 shows a simplified piping and instrument diagram (P&ID) for the pilot unit. The pilot unit is heat traced and instrumented for temperature, pressure drop and flow rate measurements for each catalyst bed. The gas flow rate through each catalyst bed is controlled independently. The pilot unit is more complex than a future full-scale implementation might be, as a full-scale implementation would not likely require any instrumentation or controls other than monitoring gas pressure drop across the catalyst.

After the pilot unit is installed and catalysts are in place, flue gas flow rates are placed in automatic control, and the unit is left to operate at least a week to allow the catalysts to come to mercury adsorption equilibrium. Then, initial oxidation performance data are collected for each catalyst. The flue gas flow rate through each chamber is varied to determine catalyst performance versus area velocity. These results are used to determine an optimum area velocity for each catalyst to achieve high initial Hg^0 oxidation efficiency (preferably greater than 90%).

Once optimum flue gas flow rates are established, the pilot unit is left in automated operation for 14 months or longer. Telemetry equipment allows pilot unit flow rate, temperature, and pressure drop data to be monitored and some control parameters to be adjusted from off site. The pilot unit is automated for all operations except mercury analyses, as described below. Otherwise, no routine operator intervention is required.

Figure 2: Simplified P&ID for the Catalyst Pilot Unit (one of four catalyst chambers shown)



On approximately a bimonthly basis, project team members travel to the site and use an EPRI mercury semi-continuous emissions monitor (SCEM) to track total Hg and Hg^0 concentrations upstream and downstream of each catalyst to determine oxidation activity. The SCEM is illustrated in Figure 3. It is based on the amalgamation of Hg^0 with gold, and cold-vapor atomic absorption of Hg^0 that is intermittently thermally desorbed from the gold. Using a liquid-phase gas conversion system, the analyzer can determine total Hg concentrations by reducing all of the oxidized mercury to the Hg^0 form with stannous chloride upstream of the gold, or only Hg^0 concentrations by using either a tris(hydroxy-methyl)aminomethane (Tris) or potassium chloride (KCl) solution to capture oxidized mercury while allowing Hg^0 to pass through unaltered.

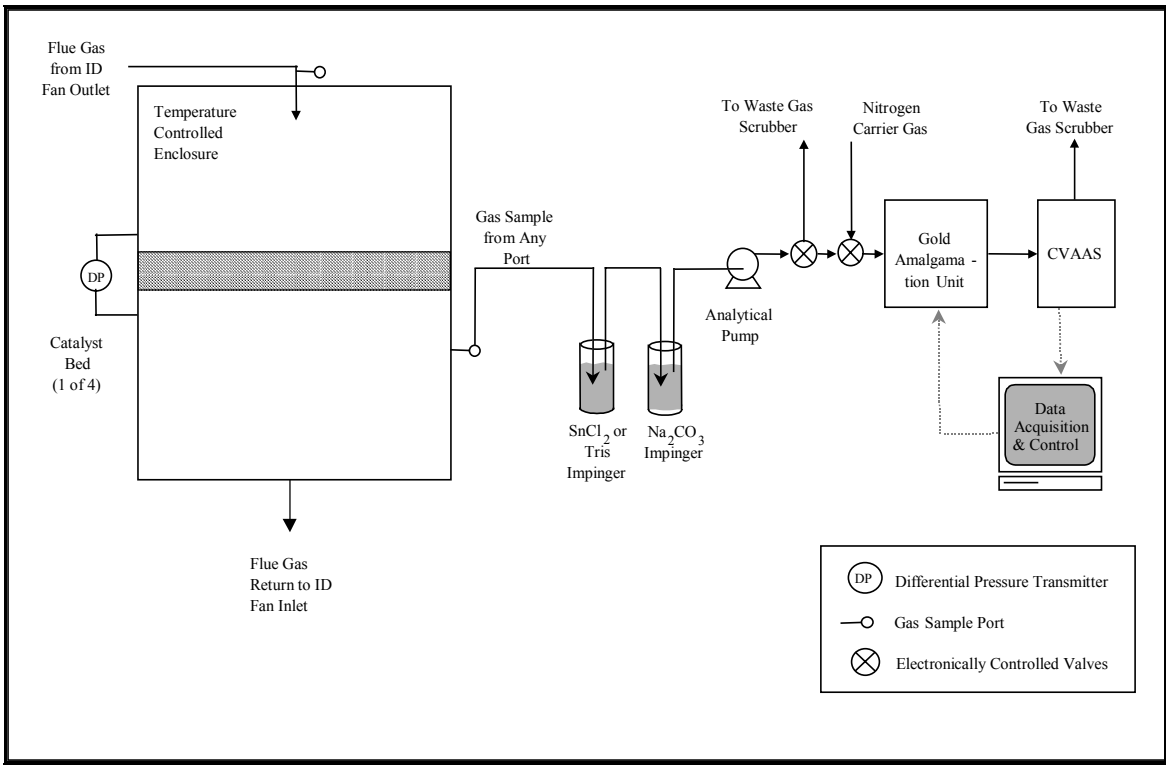
Three times over the test period at each site, flue gas measurements are conducted using the Ontario Hydro method (ASTM D6784-02) to verify results from the SCEM. Measurements are also made for sulfuric acid and NO_2 concentrations upstream and downstream of each catalyst to quantify whether the oxidation catalysts also oxidize flue gas SO_2 or NO. Significant oxidation of either would be undesirable due to plume opacity and/or corrosion effects.

At the beginning of testing at each site, a thorough characterization of the pilot unit inlet flue gas is conducted. This includes mercury concentrations and speciation by the Ontario Hydro method, halogen species by Method 26a, and trace metals by Method 29. Ontario Hydro method measurements are also conducted at the host unit FGD outlet, so the removal of mercury by species across the existing scrubber can be quantified.

Concurrently, samples of the coal, fly ash, scrubber liquor, and scrubber byproduct are collected and analyzed for mercury content, to allow a mercury balance to be calculated across the host site and to verify the fate of mercury absorbed in the host site FGD system. Also, the FGD byproducts are being evaluated in the laboratory for mercury stability.

The two host sites for the initial project, GRE's CCS and CPS' Spruce Plant, each fire low-sulfur, low-chloride coals. CCS fires North Dakota lignite with about a 6300 Btu/lb heat content, 0.7 wt% sulfur content, 0.1 ppm mercury content, and 100 ppm or less chloride content. Spruce

Figure 3: Schematic of the EPRI SCEM



fires a Wyoming, PRB subbituminous coal with about 8400 Btu/lb heat content and 0.5 wt% sulfur content. The mercury and chloride contents of the Spruce coal are similar to those at CCS (0.1 ppm mercury and less than 100 ppm chloride).

The two sites are somewhat similar in equipment configuration. Both have tangentially-fired boilers rated at about 550 net MW (two units at CCS, one at Spruce). CCS has a large cold-side ESP for particulate control, followed by ID fans and an Alstom wet lime FGD system. The FGD absorbers (open spray towers) operate at greater than 90% SO_2 removal efficiency. About 30% of the flue gas at the ID fan exit bypasses the FGD system, producing a reheat effect. At Spruce, a reverse-gas fabric filter is used for particulate control, followed by ID fans and an Alstom wet limestone FGD system. As at CCS, the absorbers are designed to achieve greater than 90% SO_2 removal, and a portion of the ID fan exit gas bypasses the FGD system. The CCS FGD system produces calcium sulfite byproduct that is landfilled, while the Spruce FGD system produces gypsum byproduct that is sold for cement production.

The new project (DE-FC26-04NT41992) has added a wet FGD pilot unit, which is sized to treat 2000 acfm of flue gas, corresponding with the flue gas treated by of one of four catalysts in the oxidation catalyst pilot unit. The wet FGD pilot unit has a spray and perforated plate tray contactor, and can be operated with either lime or limestone reagent, and with natural or forced oxidation. The pilot wet FGD does not have reagent preparation equipment, nor does it have byproduct dewatering equipment. In most instances, reagent prepared by the host site wet FGD system will be used as makeup to the pilot wet FGD.

Oxidation catalyst pilot testing has recently been completed at CCS. This paper presents field data from approximately 20 months of catalyst operation there, as well as preliminary wet FGD pilot and catalyst regeneration test results. The second, EPRI-built oxidation catalyst pilot unit has been in operation at Spruce since last fall, so approximately 8 months of catalyst operating data from that site are presented here.

RESULTS

Catalyst Supply

A bench-scale laboratory evaluation of candidate catalysts was conducted in URS' Austin, Texas laboratories, using a mixture of bottled gases intended to simulate the flue gases at CCS and Spruce. The results were used to determine which candidate catalysts were most active under these simulated flue gas conditions, and to estimate the amount of each catalyst required to achieve high Hg^0 oxidation percentages in the pilot unit. The overall dimension requirements were predicted from the laboratory results by a mass transfer model developed by URS. Table 1 shows the catalyst dimensions used in the two pilot units.

Table 1. Catalyst dimensions selected for the pilot units.

Catalyst Type	Pilot Unit	Cell Pitch (mm)	CPSI (cells per $in.^2$)	Catalyst Cross-section (in. x in.)	Catalyst Length (in)	Area Velocity (sft/hr)
SCR Catalyst	CCS	3.7	46	35.4 x 35.4	19.7	14
SCR Catalyst	Spruce	3.7	46	35.4 x 35.4	29.5	13
Experimental Activated Carbon (C #6)	CCS and Spruce	3.2	77	36 x 36	9	27
Fly-ash-based (SBA #5)	CCS	3.2	77	36 x 36	9	27
Palladium-based (Pd #1)	CCS and Spruce	3.2	64	30 x 30	9	49
Gold-based (Au)	Spruce	3.2	64	30 x 30	9	49

Argillon GmbH (formerly Siemens) supplied the SCR catalysts. Because the SCR catalyst proved to be less active at CCS than was expected, the catalyst length was increased by 50% for the Spruce pilot unit.

The Pd #1 catalysts were ordered from Sud-Chemie Prototech, who prepared three 3-in.-deep catalyst layers for each pilot unit. The C#6 and SBA #5 catalysts were custom-prepared by a U.S.-based catalyst manufacturer, as extruded monoliths in an alumina substrate. Figure 4 is a photograph of one 6-in. by 6-in. by 3-in. deep block from the SBA #5 extrusion. The catalyst vendor prepared enough blocks of this size with the SBA #5 material to produce composite catalyst layers of the overall dimensions shown in Table 1. Figure 5 shows an overall view of one of the three SBA #5 catalyst cans that were installed in the pilot unit at CCS.

For the preparation of the C #6 catalyst, two separate lots of C #6 material were activated by the Illinois State Geological Survey and MaxWell Engineering and Consulting, then ground to size for extrusion. The extrusion, drying, firing and canning of these catalyst blocks were completed in March 2003 for the catalysts installed at CCS and October 2003 for the Spruce catalysts.

Figure 4: Sample Catalyst Block for SBA #5, as Prepared by Catalyst Manufacturer

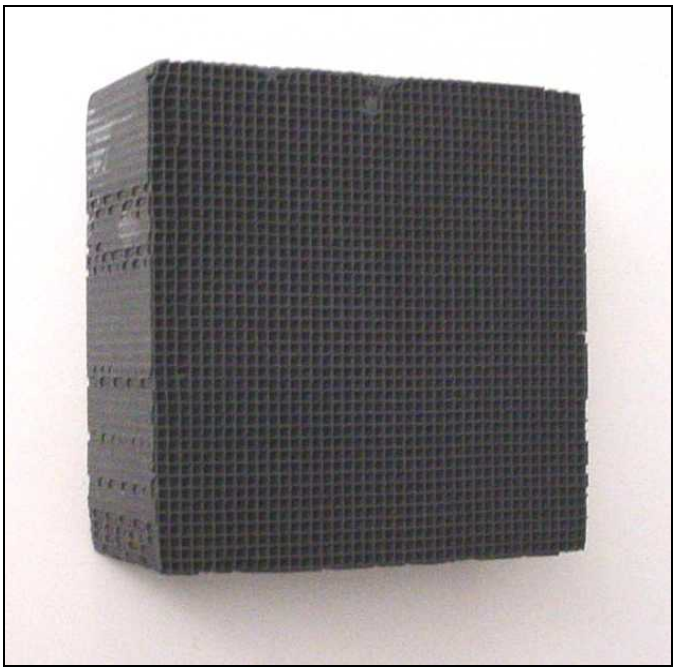


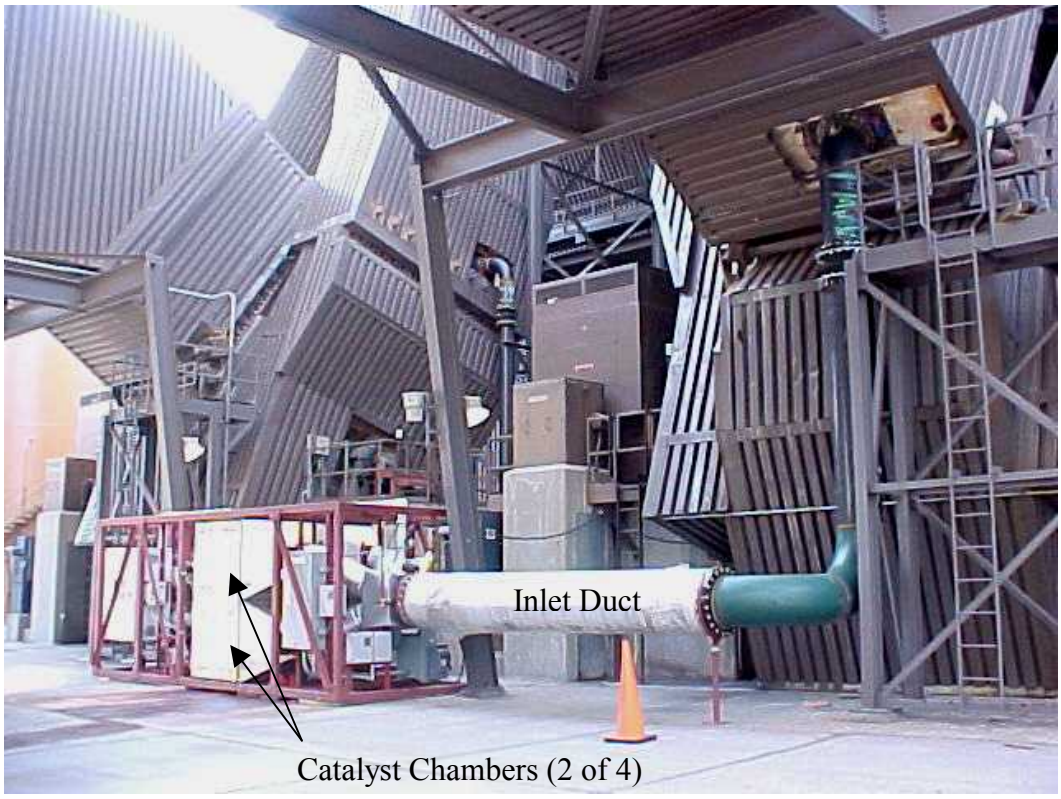
Figure 5: Photograph of One of Three SBA #5 Catalyst Cans

Gold is being tested at Spruce in the place of the SBA #5 catalyst, which was seen as being unsuitable for commercial catalyst production since it reflects unique properties of the fly ash from a single coal-fired unit. The Tennessee Valley Authority (TVA) has patented the use of gold as a mercury oxidation catalyst in coal-fired flue gases. TVA cost-shared the purchase of the gold catalyst, which was prepared by Sud-Chemie Prototech in dimensions identical to those of the Pd #1 catalysts.

Pilot Unit Operation at CCS

The pilot unit was started up at CCS in September 2002. The first two catalysts (SCR and Pd #1) were installed in early October and long-term evaluation of those catalysts began. Figure 6 is a photograph of the pilot unit as installed at CCS.

Figure 6: Oxidation Catalyst Pilot Skid as Installed at CCS



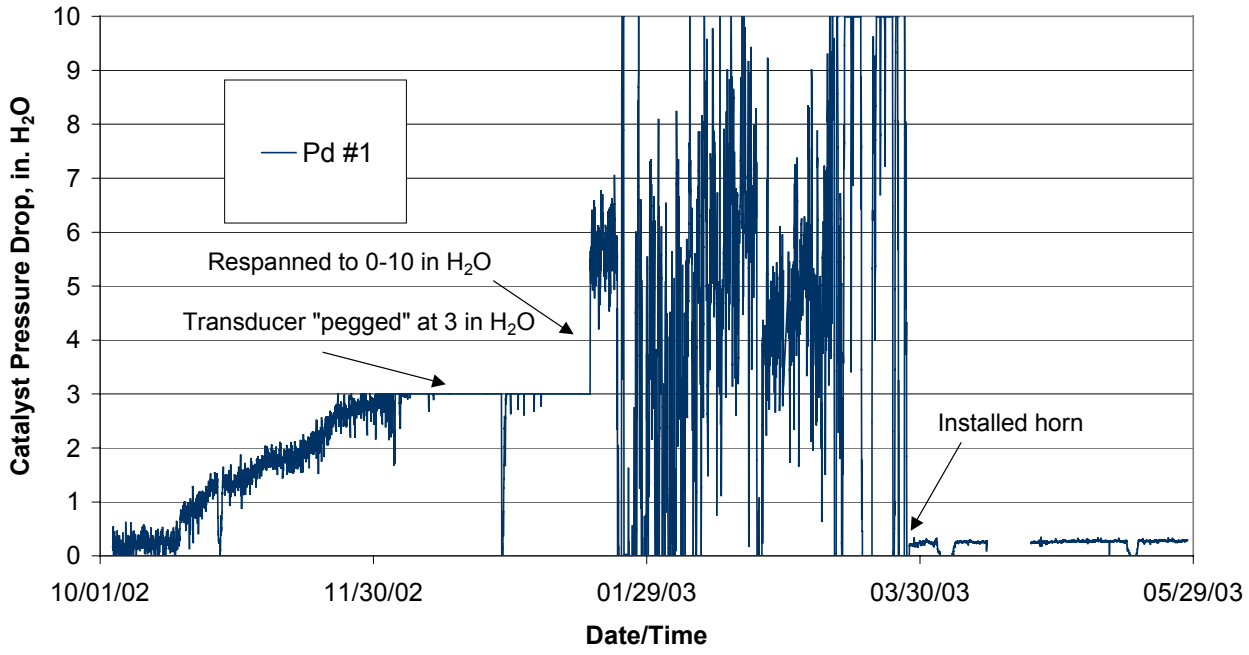
The other two catalysts (SBA #5 and C #6) were not yet available. Initial catalyst activity measurements, by mercury SCEM, showed over 90% oxidation of Hg^0 across the Pd#1 catalyst, while the SCR catalyst results showed lower oxidation, in the range of 60 to 70% across that catalyst. Throughout this paper, Hg^0 oxidation percentages across catalysts are reported based on the measured decrease in Hg^0 concentration across the catalyst, and do not just reflect the total flue gas mercury oxidation percentage at the catalyst outlet.

In December 2002, the third catalyst, SBA #5, was installed and activity measurements were made. Those results showed a marked decrease in activity for both the Pd #1 and SCR catalysts. Testing in January 2003 determined that the catalyst surfaces were becoming plugged due to buildup of fly ash in the horizontal-gas-flow catalyst cells, in spite of the catalysts being installed downstream of a high-efficiency ESP. This was confirmed by tracking pressure drop increases across the catalysts and by physically inspecting the catalyst chambers to observe and clean out the fly ash buildup.

It appeared that mechanical catalyst cleaning would be needed on the pilot unit for the horizontal-gas-flow catalysts. Both air soot blowers and sonic horns were considered. It was decided that a sonic horn would be the easiest field retrofit and would offer a good probability of success. A small, 17-inch horn produced by Analytec Corporation of Pagosa Springs, Colorado appeared to be the best solution based on price, availability, and probability of success. During the last week of March 2003, the sonic horn was installed on the Pd #1 catalyst box to provide acoustic energy to the catalyst to dislodge accumulated particulate matter. The horn was installed on the top wall of the catalyst housing inlet transition, approximately 1.5 feet upstream of the first catalyst module. The horn sounds for 10 seconds every half hour. When the sonic horn was installed, the Pd #1 catalyst modules were also manually cleaned.

The pilot unit was placed back in service, and the horn proved to be effective at controlling pressure drop across the Pd #1 catalyst. Pressure drop data for the Pd #1 catalyst for during this time period are plotted in Figure 7.

Figure 7. Pressure drop data for Pd #1 catalyst before and after sonic horn retrofit.



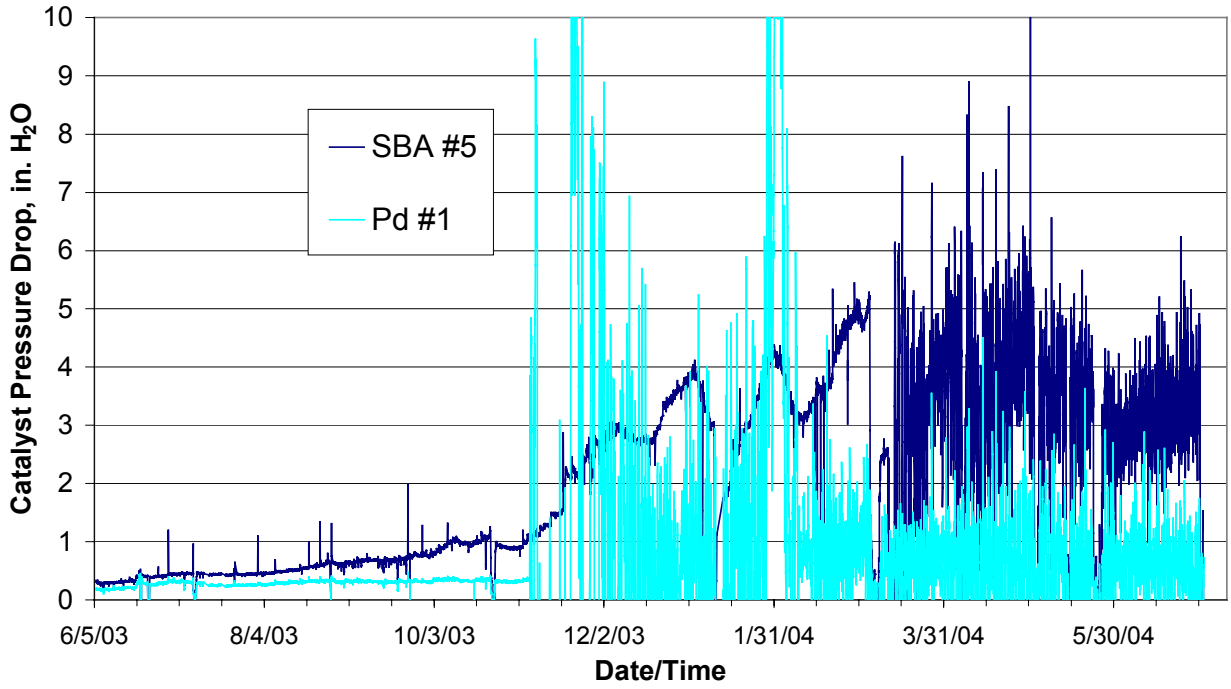
A catalyst activity measurement trip was conducted one month after the horn was put in service. The results showed high (~90%) Hg^0 oxidation across the catalyst. Based on the relatively high activity and low pressure drop values for Pd #1, sonic horns were installed on the other three boxes the first week of June 2003. The fourth catalyst, C #6, was installed in June after the sonic horn was retrofitted to that catalyst compartment.

Catalyst Pressure Drop Results

With the horns in service, the pressure drops across three of the four catalysts appear to have remained low in over one year of operation. However, the electronic signals for pressure drop across all four catalyst boxes have become very noisy, which makes the data more difficult to analyze.

Pressure drop values since the sonic horns were installed June 5, 2003 are plotted for the Pd #1 and SBA #5 catalysts in Figure 8. If all four catalyst pressure drop values were plotted, the plot would become indecipherable due to the noisy signals. However, the data plotted in Figure 8 illustrate the difference in performance between the one catalyst that has not been kept clean by the sonic horn (SBA #5) and the other three that have (as illustrated by the Pd #1 data).

Figure 8: Pressure Drop Data for Two Catalysts in Service at CCS through June 2004



The SBA #5 pressure drop has increased over time, and averaged between 3 and 5 in. H_2O during the last several months of operation. This is more than ten times the initial pressure drop on June 5, 2003. It appears that there is a particle-to-particle attraction between the fly ash in the flue gas treated and the fly ash imbedded in the catalysts. This catalyst type is of lesser interest for future commercial applications, so regardless of the cause, the pressure drop increase across this catalyst chamber is not of great concern.

As seen in Figure 8, the average pressure drop across the Pd #1 catalyst remains below 1 in. H_2O, indicating the effectiveness of the sonic horn in preventing fly ash buildup across this catalyst. The other two catalysts appear to have similar pressure drop values to those of Pd #1.

Catalyst Activity Results

The "clean catalyst" activity results for all four catalysts are plotted versus time in Figures 9 and 10. Some data points from late 2002 and early 2003, where the catalysts were obviously plugged with fly ash, have been edited from the plots. Activity results for the Pd #1 and C #6 catalysts are plotted in Figure 9 and results for SBA #5 and SCR catalysts in Figure 10.

Within the range of measurement variability, the data plotted in Figure 9 show a linear downward trend in catalyst activity versus time in service for the two more active catalysts. The June 2004 measurements are considered the "end of test" activity for the catalysts being tested at CCS, so the linear least squares fit of these data shown in the figure will be used to make catalyst life projections.

The data plotted in Figure 10 show relatively "flat" activity performance for the SCR catalyst over time since the sonic horns were installed last June, albeit at relatively low oxidation percentages. The apparent activity of the SBA #5 catalyst has continually decreased with time since September 2003, most likely due to fly ash build up across this catalyst.

Figure 9: Activity for Hg^0 Oxidation versus Time for Pd #1 and C #6 Catalysts at CCS

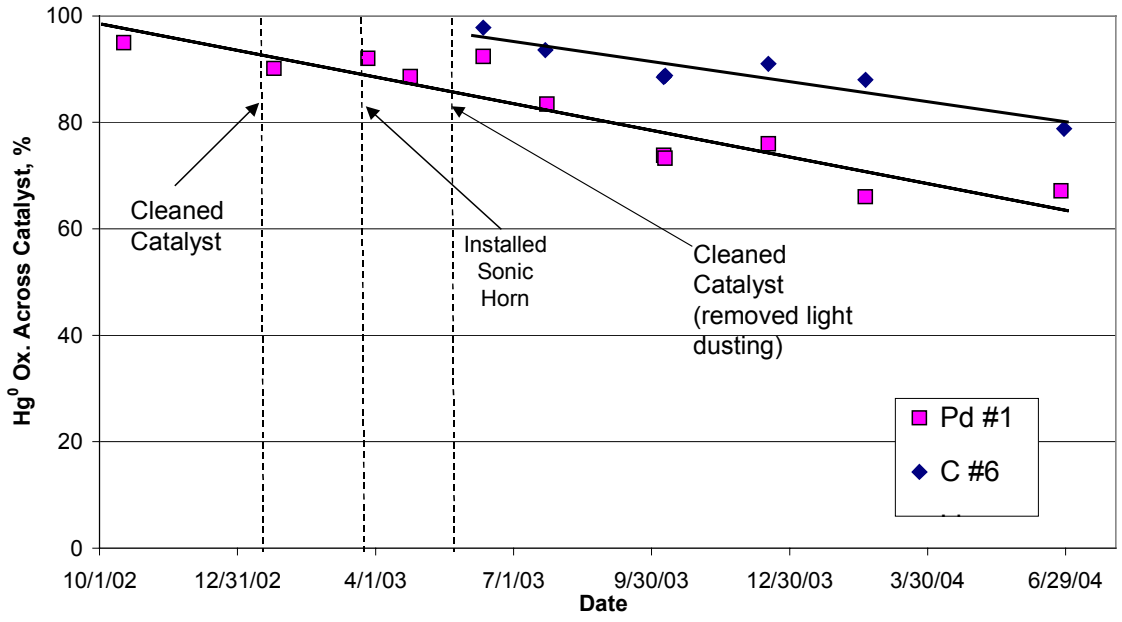
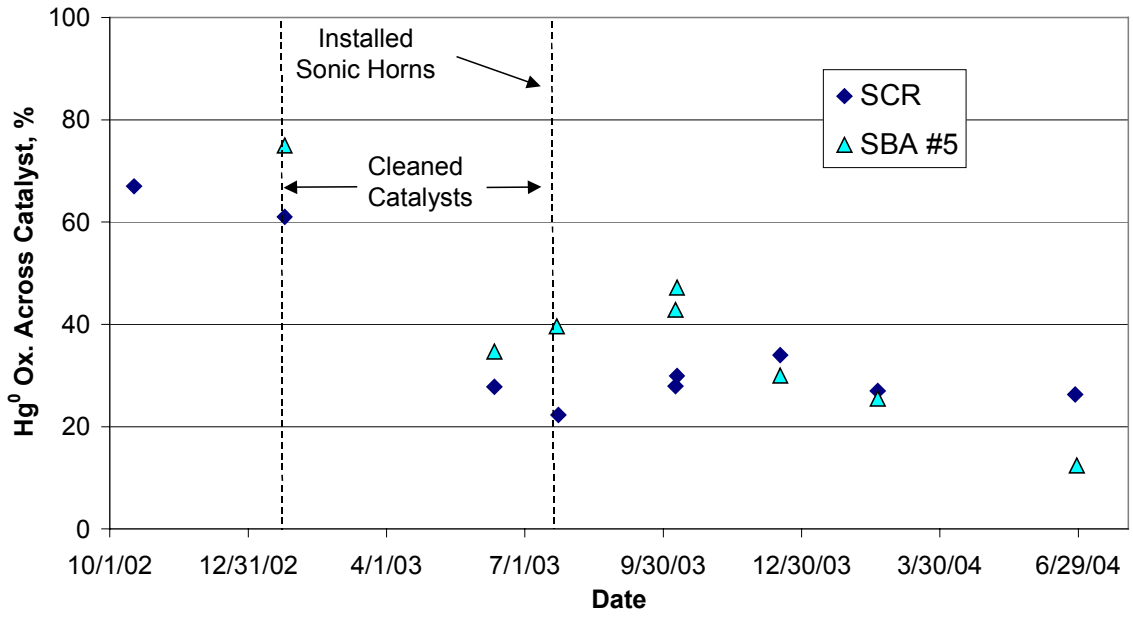


Figure 10: Activity for Hg^0 Oxidation versus Time for SCR and SBA #5 Catalysts at CCS



In late July, attempts were made to thermally regenerate the SCR and Pd #1 catalysts. After a period of heating each catalyst with 600°F air, catalyst activity was tested again on flue gas to determine if the Hg^0 oxidation activity was measurably increased. Although these results are just now being reduced and details are not available to be included in this paper, in general, it can be stated that the Hg^0 oxidation capacity of the two catalysts improved after a few hours of thermal regeneration. For example, the Hg^0 oxidation across the Pd #1 catalyst recovered to approximately 88% after regeneration. Details of these data should be available for the presentation.

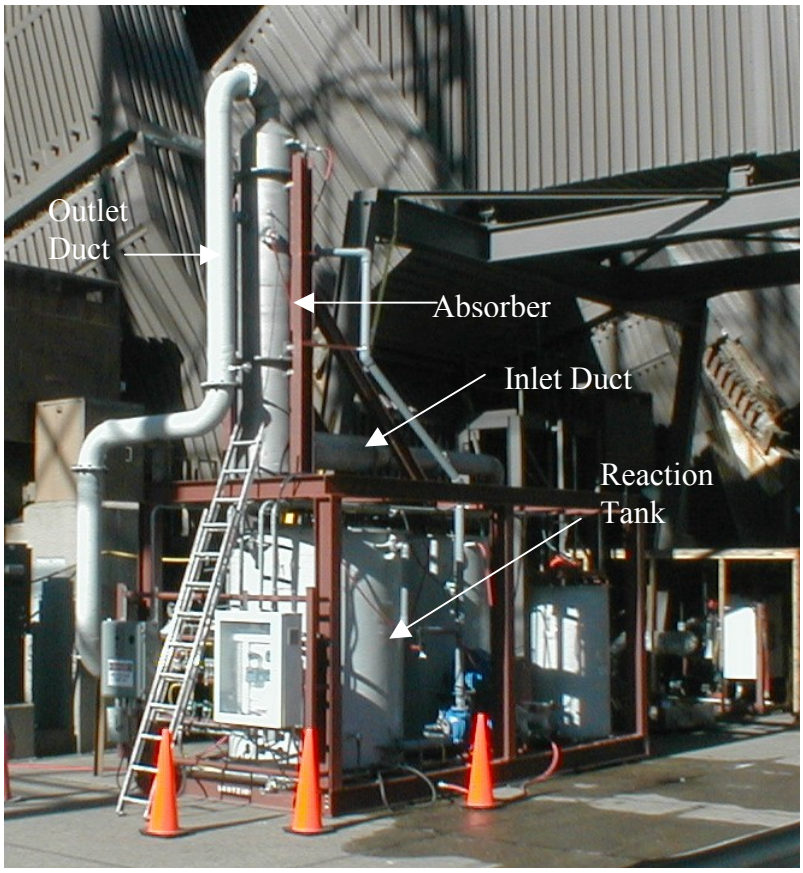
Also in July, the pilot wet scrubber was installed at CCS and used to treat flue gas under baseline (no catalyst) conditions and treating flue gas from downstream of the two more active catalysts (C #6 and Pd #1). Figure 11 shows the FGD pilot installed at CCS. The oxidation catalyst pilot is shown in the background, to the right of the pilot FGD in the photo, although it is difficult to make out any details of the oxidation catalyst skid because of the plywood structure that was erected around it for weather protection.

Again, these tests have just recently been completed, and results are not available to be included in this paper. It can, however, be said that catalytically oxidized mercury was measured to have been removed at high efficiency (>90%) across the wet FGD system. As for the catalyst regeneration results, it is expected that these pilot FGD mercury removal data will be available for the presentation.

Pilot Unit Operation at Spruce Plant

The pilot unit was started up at Spruce Plant in late August 2003 and operated with the Pd #1 and Au catalysts installed for most of September. The host unit came off line for a fall outage on September 26, and the outage continued until late October. The two remaining catalysts (SCR

Figure 11: Wet FGD Pilot Unit Installed at CCS



and C #6) were installed in the pilot unit and the pilot unit was restarted on November 13, about two weeks after the host unit came back on line. The unit has operated continuously with all four catalysts on line since then.

Pilot unit inlet flue gas Hg^0 concentrations have been much lower than were expected, given that Spruce fires PRB coal. The low Hg^0 concentrations have been attributed to mercury oxidation and removal across the reverse-gas fabric filter used for particulate control on the Spruce unit. The week of January 5, two SCEMs were taken to the site and used to measure flue gas total Hg and Hg^0 concentrations at the fabric filter inlet and outlet, and at the wet FGD outlet locations on the host unit. These measurements were made to develop a baseline characterization of host unit flue gas mercury conditions prior to rebagging the Spruce reverse-gas fabric filter with new bags. The rebagging began on January 12, and was completed at the end of February.

Catalyst Pressure Drop Results

The pressure drops across the four catalyst chambers at Spruce have remained nearly constant between 0.2 and 0.3 in H_2O. It does not appear that sonic horns will be required to prevent fly ash buildup, most likely because a high-efficiency reverse-gas fabric filter is used for particulate control at this site. The use of a fabric filter results in a low dust loading in the pilot unit inlet

flue gas, and a dust loading that has less residual electrostatic charge than would flue gas downstream of an ESP.

Catalyst Activity Results

The most recent set of catalyst measurement trip results are presented below, from May 2004, in Table 2.

Table 2. May oxidation catalyst activity results for Spruce pilot (measured by Hg SCEM).

Location	Total Hg (μg/Nm^3, corrected to 5% O_2)	Elemental Hg (μg/Nm^3, corrected to 5% O_2)	Apparent Total Hg Adsorption Across Catalyst, %	Apparent Hg^0 Oxidation Across Catalyst, %	Overall Hg Oxidation Percentage
Pd #1 Inlet	10.7	1.89	-	-	82
Pd #1 Outlet	9.91	0.12	7	94	99
C #6 Inlet	10.3	2.01	-	-	80
C #6 Outlet	10.3	0.19	0	91	98
Au Inlet	11.1	2.75	-	-	75
Au Outlet	10.5	0.21	5	92	98
SCR Catalyst Inlet	10.8	2.30	-	-	79
SCR Catalyst Outlet	11.2	0.13	0	94	99

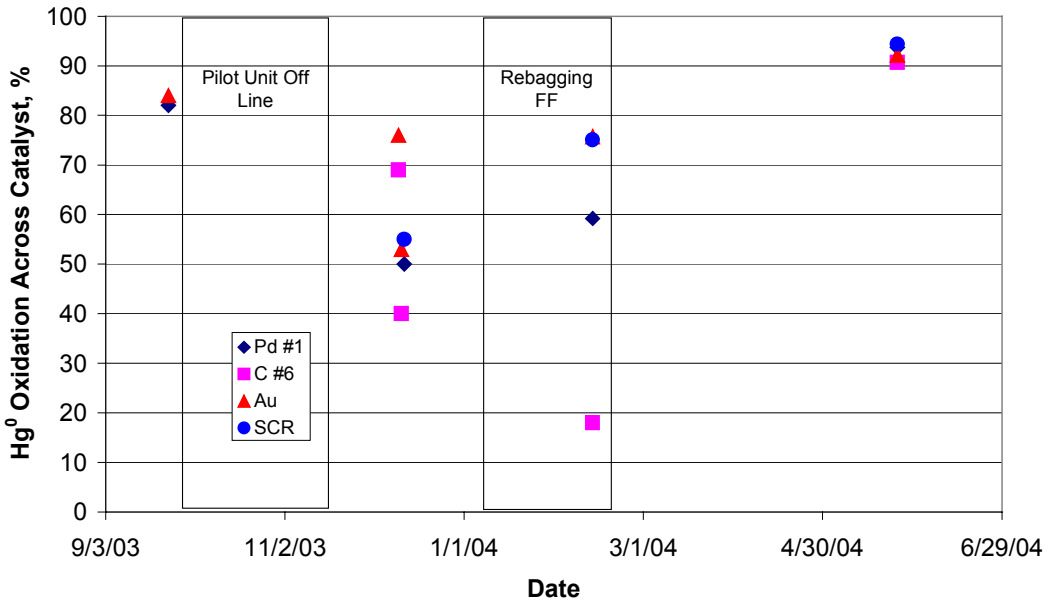
As has been seen in previous measurements at Spruce, the pilot unit inlet flue gas showed high mercury oxidation percentages, with SCEM measurements showing 75 to 82% oxidized rather than the expected 20 to 30% oxidized mercury typical of PRB flue gases. This effect appears to be an influence of the fabric filter used for particulate control. The fabric filter operates at a low air-to-cloth ratio (less than 1.5 acfm/ft^2) and at flue gas temperatures below 300^{o}F. The fabric filter rebagging in January/February had little apparent effect on mercury oxidation across the baghouse. In May, with new bags, baghouse outlet Hg^0 concentrations were measured to range from 1.9 to 2.8 μg/Nm^3, which are not at high as would be desired from the standpoint of being able to measure oxidation catalyst performance.

Measurement of catalyst activity at Spruce is difficult for two reasons. One is that because of mercury oxidation and capture across the fabric filter, the Hg^0 concentrations at the oxidation catalyst pilot unit are relatively low, typically less than 3 μg/Nm^3 as mentioned above. This means that for well performing catalysts, the catalyst outlet Hg^0 concentrations are less than 1 μg/Nm^3, a low concentration that is difficult to measure accurately with the mercury SCEM (or by any other method). The second difficulty is that the pilot inlet total and Hg^0 concentrations can change significantly throughout the day, perhaps being impacted by factors such as fabric filter pressure drop and compartment cleaning cycles. A single Hg SCEM is normally used to quantify catalyst performance and must cycle between the pilot inlet flue gas sample and the catalyst chamber outlet samples, so inlet concentration variations can markedly impact observed mercury adsorption and elemental mercury oxidation percentages.

Because of these previous difficulties in measuring catalyst performance, two mercury SCEMs were used during the May trip, one dedicated to measuring inlet mercury concentrations while the other cycled through the four catalyst chamber outlets. URS' newest, highest resolution analyzer was used for measuring the catalyst outlets, and increased measurement cycle times were employed so that the amount of mercury captured on the analyzer gold trap was above the low instrument calibration standard. With this approach taken for measuring catalyst performance, it appears that all of the catalysts are performing well, with each measuring greater than 90% oxidation.

All of the catalyst activity results measured by SCEM at Spruce since September 2003 are plotted in Figure 12. The catalyst activity results show quite a bit of variability over time, and during some measurement periods the apparent mercury oxidation percentages are much lower than expected, and much lower than were measured later. It is believed that these low oxidation percentages represent measurement anomalies related to the low and variable inlet Hg^0 concentrations. The data from the May measurement trip, which are believed to be the most reliable, show that all four catalysts are achieving greater than 90% oxidation of the inlet elemental mercury. The next measurement trip is scheduled for August, and will provide an opportunity to see whether the high activity results measured in May, with the improved measurement approach, will be repeated.

Figure 12: Catalyst Activity versus Time in Service at Spruce Plant



Future Testing

For the current project, testing has been completed at CCS, and the oxidation catalyst pilot unit is scheduled to be moved to TXU Energy's Monticello Steam Electric Station in Mount Pleasant, Texas sometime in August. TXU will be hosting pilot catalyst tests and intermittent wet FGD

pilot tests at Monticello, which fires a Texas lignite/Power River Basin (PRB) coal blend. The TXU test program will continue through approximately the end of calendar year 2005.

The second pilot unit is scheduled to continue operation at Spruce Plant through the end of calendar year 2004. During the fall, pilot wet scrubber tests will be conducted downstream of the oxidation catalysts at Spruce. The original plan for the 41992 project was that the catalyst pilot unit at Spruce would be shipped to a Duke Energy bituminous coal fired plant after the Spruce tests are completed, either their Marshall or Allen plant. However, flue gas testing at these plants has indicated very low Hg^0 concentrations at the ESP outlet (less that 2 $\mu g/Nm^3$), making these sites unsuitable for testing Hg^0 oxidation catalysts. Consequently, the project is seeking a new co-sponsor and site to host oxidation catalyst pilot and wet FGD pilot tests, preferably a site firing a low-sulfur Eastern bituminous coal.

SUMMARY AND CONCLUSIONS

The mercury oxidation catalyst pilot unit has been designed, built and installed; catalysts were selected, sized and procured; and the pilot unit has operated approximately 20 months at CCS. During this period of operation at CCS, catalyst activity for Hg^0 oxidation was measured numerous times and the flue gases on the host unit and around the pilot unit were characterized by manual gas sampling methods.

The Pd #1 and C #6 catalysts have proven to be the more active catalysts at CCS, with the Pd #1 achieving greater than 65% Hg^0 oxidation after 20 plus months of operation and the C #6 catalyst achieving approximately 80% oxidation after 13 months of operation. Preliminary results suggest that the Pd #1 can be readily regenerated to improve oxidation activity by heating to about 600^oF for a period of several hours. Preliminary results also suggest that Hg^0 catalytically oxidized across the Pd #1 and C #6 catalysts can be removed by a wet FGD absorber at high efficiency.

In this 20 plus months of pilot unit operation, it has become apparent that the potential for adverse effects from the ash remaining in the flue gas downstream of a high-efficiency ESP was underestimated. After two months of operation, the Pd #1 and SCR catalysts had seen a significant loss of activity for Hg^0 oxidation and a significant increase in pressure drop. Because of the observed ash accumulation on the catalysts at CCS, sonic horns were installed and operated on the catalyst chambers for over one year, and appear to be effective in limiting fly ash build up for three of the four catalysts. Only the fly-ash-based catalyst, which is of relatively little interest as a commercial catalyst material, was not kept clean by the sonic horn.

Gas sampling results (not presented in this paper) show negligible oxidation of SO_2 to increase sulfuric acid concentrations in the flue gas across the mercury oxidation catalysts, and no measurable oxidation of NO to NO_2. These are both positive results, as significant oxidation of either of these species across the mercury oxidation catalysts could have produced undesirable balance-of-plant effects.

Results to date from Spruce plant show that sonic horns may not be necessary to keep the horizontal gas flow catalysts clean when installed downstream of a reverse-gas fabric filter. However, the fabric filter has also been observed to oxidize and remove a significant fraction of

the Hg^0 in the air heater outlet flue gas from the PRB-fired unit. This makes it difficult to evaluate the Hg^0 oxidation activity of the catalysts being evaluated there. The most recent field data show that all four catalysts are achieving greater than 90% Hg0 oxidation after six to seven months in service.

REFERENCES

1. *Enhanced Control of Mercury by Wet Flue Gas Desulfurization Systems, Final Report, Phase II,* Award No. DE-AC22-95PC 95260, U.S. Department of Energy National Energy Technology Laboratory, Pittsburgh, PA: 2001.